Protecting Puget Sound Watersheds from Agricultural Pollution Using a Progressive Manure Application Risk Management (ARM) System

Standard Operating Procedure (SOP) for:

THE COLLECTION SURFACE WATER SAMPLES

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1. SCOPE AND APPLICABILITY

The purpose of this Standard Operating Procedure (SOP) is to establish a uniform, consistent procedure for the installation of pan and tension lysimeters as well as the collection of soil water samples from those lysimeters. The procedures outlined in this SOP pertain to all project personnel that conduct field sampling associated with this project.

2. SUMMARY OF METHOD

Surface water is collected by two methods, overland flow and in-stream sampling. Overland flow collection is conducted using in-ground flow collection vessels from which samples can be collected and assessed. In stream collection will be conducted in streams, ditches, creaks, etc., adjacent to test fields using immersed sample bottles. Each method will be analyzed both in-field with a handheld probe and by a laboratory.

3. HEALTH & SAFETY WARNINGS

Concentrated strong acids (sulfuric) used to preserve samples are corrosive and toxic. Care must be taken when handling them. Wear gloves and protective eyewear when working with concentrated acids.

4. PERSONNEL QUALIFICATIONS/RESPONSIBILITIES

All project personnel performing field equipment installation and sample collection must go through in-house training on sampling equipment and procedures outlined in this SOP.

5. EQUIPMENT AND SUPPLIES

The following section outlines the construction, set-up, and sampling procedures of the overland flow sampler, as well as all the sample containers, field equipment, and field supplies needed for successful operation of project procedures.

5.1. Overland Flow Collector Set-Up

The overland flow collector is constructed out of a 2 gallon HDPE plastic bucket (Paragon MFG, Inc., Melrose Park, IL) with a modified HDPE lid (Figure 1). The lid has been modified by drilling a pattern of 5/16 inch holes into the top for drainage into the bucket. A layer of 50 micron polyester filter felt, topped with a layer of 0.080 x 0.055 inch opening polypropylene plastic mesh, are attached with silicone to the top of the lid. When installed in the soil profile, the 1/4 inch recession of the lid is filled with clean, inert sand.

Vent and collection ports, inserted approximately 6 inches from the bottom of the bucket, consist of a 1/4 inch polyethylene barbed elbow fitting on the outside of the bucket and a 1/4 inch nylon

female barbed tube fitting on the inside. A 0.078 inch thick Santoprene sealing washer with a 0.04 inch thick stainless steel shim is inserted between the bucket and the fitting on both the inside and outside of the bucket for leak protection. Tygon tubing, 1/4 ID, 7/16 OD (R-3603), is attached to the barbed fittings with a tensioned zip-tie in the inside and outside of the sample port and the outside of the vent port. The tubing on the inside of the collection port reaches all the way to the bottom of the bucket to obtain the entire sample. Tubing clamps (340TC; Halkey Roberts) keep the Tygon tubing sealed when not in use.

Sample collection is conducted by attaching the 1/4 inch Tygon sample tube to a 500 ml Polypropylene Nalgene Filtering Flask via a 1/4 inch nylon barbed tube coupling fitting. The flask is put under vacuum (Model 2005G2 Vacuum Hand Pump; Soilmoisture Equipment Corp, Santa Monica, CA) and the sample inside the bucket is collected into the flask. The sample is then transferred into the appropriate sample container (see Sample Containers).

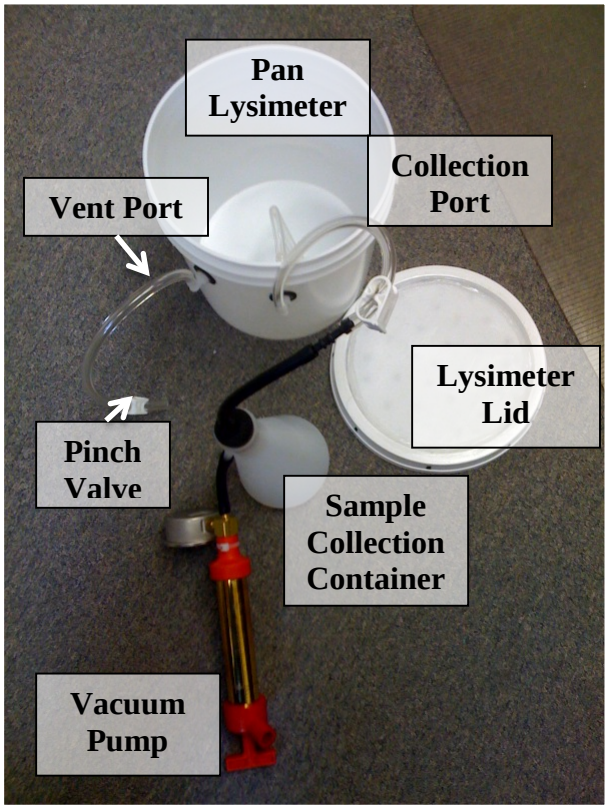

Figure 2. Overland flow collector set-up. The pan lysimeter is a three gal bucket with a modified, felt and polypropylene covered top, and 0.25 inch ports for venting and sample collection.

5.3. Sample Containers

All sample containers will be clean and sterile and supplied by the testing laboratory (Exact Scientific Services, Bellingham, WA).

- Fecal coliform – 125 ml Nalgene HDPE wide-mouth bottle
- Comprehensive sample to lab – 250 ml or 1000 ml Nalgene HDPE wide-mouth bottle
- In-situ field sample – 500 ml Nalgene HDPE wide-mouth bottle (minimum 1.75 inch mouth)

5.4. In-Situ Field Equipment

5.4.1. In field sampling equipment

- YSI Professional Plus (YSI Incorporated, Yellow Springs, OH) handheld multiparameter instrument for measurement of temperature, dissolved oxygen, electrical conductivity, ammonium, and nitrate.
- EcoSense pH10 pH/Temperature Pen (YSI Incorporated, Yellow Springs, OH) for measurement of pH and temperature.

5.4.2. Calibration standards

- Ammonium – 1 mg/L and 100 mg/L (North Central Labs, Birnamwood, WI)
- Nitrate - 1 mg/L and 100 mg/L (North Central Labs, Birnamwood, WI)
- Conductivity – 1000 microsiemens/cm (YSI Incorporated, Yellow Springs, OH)
- pH – Buffer solution 4.00, 7.00 and 10.00 (North Central Labs, Birnamwood, WI)

5.5. Field Supplies

- Field log book (Model 310 & 350; Rite in the Rain, Tacoma, WA)
- Field pens and pencils
- Enviro-Safe Thermometer -20° to 110°C, Partial Immersion (calibration traceable to NIST standards) (H-B Instrument Company, Collegeville, PA)
- Cooler
- Ice
- Wash bottle – 1000 ml Nalgene LDPE wide-mouth wash bottle
- Deionized (DI) water
- Syringe, 30 ml (polypropylene, luer lock; Becton Dickinson, Franklin Lakes, NJ)
- Sulfuric Acid
- Pipette (1 ml)
- Gloves
- Protective eyewear
- Graduated cylinder (100, 500, and 1000 ml polypropylene; Bel-Art Products, Pequannock, NJ)
- Clean sand
- Tennis ball
- Stopwatch
- 51 inch container holder (Nifty Nabber, Unger Industrial, LLC, Bridgeport, CT)

6. PROCEDURAL STEPS

The following information outlines the steps necessary for instrument calibration, sample collection, sample handling and preservation, in-field sampling, and labeling.

6.1. Instrument Calibration

Prior to use each sampling day, all equipment should be calibrated using known standards (5.4.2).

For the YSI Professional plus meter, calibration should be checked for the dissolved oxygen, conductivity, nitrate, and ammonium probes following manufactures guidelines (Appendix A). If the instrument is within ±2% for dissolved oxygen, ±10% for ammonium or nitrate, and ±0.5% for conductivity (the instrument error values), no calibration is needed. If the value is outside of that range, conduct a two point calibration following the YSI instrument calibration instructions (Appendix A).

For the pH meter, calibration checks should be conducted prior to each sampling use. Conduct the check with the pH 7 solution first. If it is within 0.1 units, no calibration is needed. If it is outside of this error, conduct a two or three point calibration following manufactures guidelines (Appendix B).

6.2. Preparation

Prior to sampling, conduct the following activities:

1. Review the specific site map to determine the location of sampling equipment and plan out sampling activities.
2. Obtain all necessary sampling and monitoring equipment and supplies. Check to make sure there are adequate quantities of supplies for the sampling effort.
3. Decontaminate and/or pre-clean equipment, and ensure that it is in working order.
4. Coordinate with field staff and landowners on timing and extent of sampling event.
5. Review the sampling and collection SOP.
6. Use GPS, stakes, flagging, or buoys to identify and mark all sampling locations prior to sampling.

6.3. Sample Collection

All sample collection is conducted following guidelines outlined by Department of Ecology (Ward, 2001) and/or the U.S. Geological Survey (USGS, 2006).

6.3.1. Overland flow Collection

1. Prior to collection, make sure that the sample collection container is clean and dry.
2. For collection of samples from the pan lysimeter, retrieve the vent and sample lines for the appropriate lysimeter (each tube should be marked with a depth and identification code).
3. Clamp the vent line.
4. Remove the clamp from the sample line and attach the sample line to the barbed hose connector on the sample collection vessel.
5. With the sample tube attached to the sample collection vessel, slowly apply vacuum to the collection vessel until the entire sample has been removed from the lysimeter. If more sample is in the pan than the collection vessel can accommodate, stop the vacuum when the liquid reaches the “max fill line”, and transfer the liquid to a sample container. Repeat until the entire sample has been removed from the lysimeter.

6. Measure the volume of sample collected using an appropriate sized graduated cylinder (rinse the cylinder with DI water before and after to use).
7. Transfer the collected sample to the appropriate labeled sample container (see 6.3 for Sample Handling and Preservation) and cap immediately. **Do not touch the inside of the container, the lip of the container, or the inside of the lid**. *If there is less than 500 ml of sample available, place in the 500 ml container, perform in-situ field tests, then send the same sample to the lab. If this is performed, be sure to send in an additional pre-sample rinsate QC check with the sample.*
8. Discard any excess sample at least 10 feet away from any sample area and 30 from waterways.
9. Disconnect the sample line and replace the hose clamp on the sample line.
10. Undo the hose clamp on the vent tube.
11. Rinse the sample line by injecting 100ml of DI water from the end of the sample line into the lysimeter. Pump out the rinse water and discard. Rinse out the collection vessel three times with DI water.

6.3.2. In-stream Sample Collection

Take upstream and downstream samples only at the points indicated on sample maps provided by the Project Manager. Each map is specific to the specific sample site.

1. First, determine the in stream flow rate. Do this by measuring off a set distance of approximately 10 feet or more (depending on length of stream segment measured). Place the ball (or any type of floating object) into the center of the flow at the start line and record the time it takes for it to reach the stop line. Record the values. The distance over the time is the flow rate (ft/sec).
2. Obtain a clean sample container.
3. Place it in the container holder.
4. Remove the lib, careful not to touch the lip of the bottle nor the inside of the lid.
5. Extend the sample bottle out into the center of the stream flow or up to 5 feet from the bank edge (do not go further than the center of the channel).
6. With the mouth of the bottle facing upstream, dip the sample bottle into the flow, approximately 12 inches below the surface (do not go deeper than halfway through the water column), until it reaches the fill line of the sample container (if overfilled, dump out the excess until it reaches the fill line).
7. Remove the container from the container holder; cap, label, preserve (if necessary), and put into the cooler.
8. Repeat for each desired sample.

6.4. Sample Handling and Preservation

6.4.1. Sample Handling

Use the appropriate sample container when obtaining samples: 125 ml (fecal coliform) 250ml (individual analysis), 1000 ml (multiple analysis), or 500 ml (in-field testing).

If there is less than 500 ml of sample available, place in the 500 ml container, perform in-situ field tests, then send the same sample to the lab. If this is performed, be sure to send in an additional pre-sample rinsate QC check with the sample.

Place all sample containers in a dark cooler maintained at 4°C ± 2°C (test every 4 hours with a thermometer and record results).

6.4.2. Preservation

Samples being tested for fecal coliform must be taken to the lab within 6 hours of obtaining them.

For any water sample that will be analyzed for total nitrogen, ammonia nitrogen, or total phosphorous, the sample needs to be acidified with sulfuric acid to a pH <2 (amount of H_2SO_4 will vary by sample size, but is generally about 0.5ml H_2SO_4/250ml (Gibbons et al., 1994); or 0.35% H_2SO_4 by weight or less) (EPA, 1990). Test the number of drops needed on one sample, record, and use that amount for the rest of the study. **Wear gloves and protective eyewear when working with concentrated acids.**

6.5. Sample Analysis (In-Field)

1. Obtain the 500 ml field sample container and insert the clean YSI Pro Plus probe into the sample. (For rinsate QC checks, take the rinse sample pre-sample, before the probe is inserted into a sample).
2. Gently move the probe up and down to remove any air bubbles.
3. Follow manufacturer guidelines in Appendix A for proper instrument operation and sample reading.
4. Once the reading is steady, record the values in both the instrument and in a log book (backup recording).
5. Discard any excess sample not being used for sample or QAQC purposes (see Section 8) at least 10 feet away from any sample area and 30 from waterways.

6.6. Labeling and Recording

All samples should follow the same labeling and recording protocol.

6.6.1. Container labeling

All sample containers will be labeled according to a code system which contains information including:

- sample type (i.e., medium, analyte, technology),
- site number,
- field number,
- date,
- and sample number (add a “D” for duplicate and “B” for blank).

6.6.2. Recorded information

All samples obtained will be recorded in ink in a bound field log book (Rite in the Rain, Tacoma, WA). Any corrections to information entered into the log book will be lined out using a single line and signed and dated by the sampler. The information recorded will include:

- date,
- time of each sample collection,
- GPS coordinates of each sample location,
- site number,
- field number,
- sample number (add a “D” for duplicate and “B” for blank),
- sample medium type,
- analysis being performed (lab or field),
- weather parameters and conditions,
- field conditions (crop, cover density, ponding, etc.),
- person performing sampling,
- laboratory sent to,
- holding time between collection and analysis.

Any other noteworthy items will also be recorded including photos taken to document field conditions and sample procedures.

7. DATA AND RECORDS MANAGEMENT

A chain-of-custody form, supplied by the laboratory, will be completed in the field at the time of sampling and submitted with samples. Both the date and time of sample relinquishment (field technician) and receiving (laboratory) will be recorded on the form. Copies of forms will be retained and given to the Project Manager.

8. QUALITY CONTROL AND QUALITY ASSURANCE

In order to identify any variability in sample collection, analysis, or measurement activity, a quality control protocol is in place. Variability will be tested for in-field using a combination of blanks, repeated measures, and duplicates to measure the effect of errors and identify areas where corrective action needs to be taken. All QC samples are sent blind to the lab.

8.1. Blanks

Field blanks will be taken to assess the background or contamination levels (variability) of various parameters such as sample containers, handling procedures, and background pollution levels.

Field blanks will represent 2% of all samples (1 per 50 samples) taken for water quality parameters. A sample container will be filled with the same clean DI water used to rinse all equipment and bottles, handled in the same environment and the same way as sample containers and sent to the lab for analysis of the same analytes as the sample it is paired with.

A rinseate blank will be taken once every 50 samples for water samples. Every 50th use, the YSI probe will be cleaned in the regular way it is cleaned between uses, then it will be rinsed with DI water, which will be collected directly into a 250 ml sample container, and sent in for analysis for all parameters. A positive value will warrant a review of cleaning procedures.

8.2. Repeated (Replicate/Split) Measures

Repeated measures (replicate and/or split samples) will be conducted to assess the imprecision (random error) of in-situ field equipment and methods, sample collection and composite sampling methods, as well as to check the accuracy of laboratory analysis.

A replicate sample will be taken every 20th sample (5% of total samples). The replicate will be taken just after the primary sample, handled in the same manner, and sent to the lab for duplicate analysis.

Water samples measured in-situ with the YSI field meter will be split into two bottles every 10th sample (10% of total samples) and both samples will be analyzed the same way with the field meter, cleaning the probe between samples. Values will be recorded in the field log book. (*This measurement is subject to sufficient volume collected by the lysimeters. If enough volume is not available for a split sample, this QC measure will be postponed until the next sample that does have sufficient volume*).

A difference of up to 30% will be accepted between samples (%Diff = (|sample 1 – sample 2|)/[(sample 1 + sample 2)/2] * 100%). If the samples differ by more than 30%, corrective action will be taken (see Table 14.1).

8.3. Accuracy (Precision & Bias)

Accuracy of field equipment will be assessed by in-field comparison to known values (i.e., known solutions, certified equipment values, etc.).

To measure the in-situ precision of the YSI field monitor, temperature, nitrate, ammonium, and pH will be compared against known solutions or certified equipment (thermometer) every 10th sample. The pH probe will be verified with a known solution of pH 7.0. The nitrate and ammonium probes will be validated against a 1 mg/L calibration solution. For temperature, a NIST certified thermometer will be inserted into the sample and compared against the instrument reading. Comparisons will be recorded in the field log book. Corrective action will be taken if any significant differences (Diff >10%) between the two methods are noted.

The temperature of the sample transport container (cooler) will be checked with a certified thermometer (Enviro-Safe Thermometer; H-B Instrument Company, Collegeville, PA) at each sample event. Temperature will be recorded in the field log book. Corrective action will be taken if the temperature is not at the specified level.

Field QC	Frequency	Acceptance Limits	Corrective Action

Field Blanks	1 per 50 samples (2%)	No false negatives or positives	New containers, new sample water, resample, or qualify data
Rinseate	1 per 50 samples (2%)	Trace or lower detection	Clean YSI meter or soil probe
Field Replicate (Duplicate)	1 per 20 samples (5%)	Within specified precision limits (RPD <30%)	Reclean, retest, SOP review, qualify data
Field Splits	1 per 10 samples (10%)	Within specified precision limits (RPD <30%)	Check monitor batteries, recalibrate field equipment
Cooler Temp	Every 4 hours of a sample event	Within specified range (3-5°C)	Adjust ice content of cooler (+/-)

9. REFERENCE SECTION

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